

TITLE OF INVENTION
DYEING OF MODACRYLIC/ARAMID FIBER BLENDS

1. Field of the Invention

5 This invention relates to dyeing of modacrylic/aramid fiber blends.

2. Description of Related Art

10 The present invention is directed to dyeing of fiber blends particularly useful in fabrics not only possessing flame resistance but also one or more additional properties. Examples of additional properties include resistance to electrical arcing, a high level of tensile strength and abrasion resistance.

15 Soiron et al. USP 4,066,395 discloses a process for dyeing or printing aromatic polyamide fibers with cationic dyes in an aqueous medium containing a carrier without ketone-forming carbonyl groups and an anionic assistant.

 Lundsford et al. USP 6,547,835 discloses a process for dyeing flame resistant fabric blends containing cellulosic fibers containing a flame retardant compound employing selected dye assistants.

20 A need is present for dyeing specific blends of flame resistant fibers without excessive shrinkage of the fibers or undue stiffness solely due to the dyeing procedure.

SUMMARY OF THE INVENTION

25 The present invention relates to a method of dyeing a blend of modacrylic fiber and aramid fiber employing a cationic dye and a dye assistant wherein the modacrylic fiber is present in a range of 1 to 99 weight % and the aramid fiber is present in a range from 99 to 1 weight % on the basis of modacrylic fiber and aramid fiber. The method comprises the step of

 contacting the fiber blend at a temperature in a range from 70 to 100 degrees C. in an aqueous dye bath containing a cationic dye and a

dye assistant present in an amount not greater than 15 grams per liter of dye bath, said dye assistant selected from the group consisting of aryl ether, benzyl alcohol, N-cyclohexylpyrrolidone, N,N-dibutylformamide, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt,

- 5 N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-octylpyrrolidone, a blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide and mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

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The starting material for the dyeing procedure of the present invention is a blend of modacrylic and aramid fibers. Normally the blend will be dyed with the fibers present as a yarn or as a yarn formed into a fabric. However it is within the scope of the dyeing procedure that the
15 blend of fibers is dyed prior to formation such as into a yarn or fabric.

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The composition of the starting material is a modacrylic/aramid blend comprising 1 to 99 weight % modacrylic fiber and 99 to 1% weight % aramid on a basis of the modacrylic and aramid components. An example of a preferred range based on these two components is 40 to 70 weight %
20 modacrylic fiber, 5 to 20 weight percent p-aramid fiber and 10 to 40 weight % m-aramid fiber. This example of a preferred range results in a blend useful in a yarn and fabric to provide electrical arcing resistance and flame protection.

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By "yarn" is meant an assemblage of fibers spun or twisted together
25 to form a continuous strand, which can be used in weaving, knitting, braiding, or plaiting, or otherwise made into a textile material or fabric.

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By modacrylic fiber it is meant acrylic synthetic fiber made from a polymer comprising primarily acrylonitrile. Preferably the polymer is a copolymer comprising 30 to 70 weight percent of a acrylonitrile and 70 to
30 30 weight percent of a halogen-containing vinyl monomer. The halogen-containing vinyl monomer is at least one monomer selected, for example, from vinyl chloride, vinylidene chloride, vinyl bromide, vinylidene bromide, etc. Examples of copolymerizable vinyl monomers are acrylic acid,

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methacrylic acid, salts or esters of such acids, acrylamide, methylacrylamide and vinyl acetate.

The preferred modacrylic fibers of this invention are copolymers of acrylonitrile combined with vinylidene chloride, the copolymer having in
5 addition an antimony oxide or antimony oxides for improved fire retardancy. Such useful modacrylic fibers include, but are not limited to, fibers disclosed in United States Patent No. 3,193,602 having 2 weight percent antimony trioxide, fibers disclosed in United States Patent No. 3,748,302 made with various antimony oxides that are present in an amount
10 of at least 2 weight percent and preferably not greater than 8 weight percent, and fibers disclosed in United States Patent Nos. 5,208,105 & 5,506,042 having 8 to 40 weight percent of an antimony compound.

As used herein, "aramid" is meant a polyamide wherein at least 85% of the amide (-CONH-) linkages are attached directly to two aromatic
15 rings. Additives can be used with the aramid and, in fact, it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the aramid or that copolymers can be used having as much as 10 percent of other diamine substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted
20 for the diacid chloride of the aramid. Suitable aramid fibers are described in Man-Made Fibers--Science and Technology, Volume 2, Section titled Fiber-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers are, also, disclosed in U.S. Pat. Nos. 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and
25 3,094,511. M-aramid are those aramids where the amide linkages are in the meta-position relative to each other, and p-aramids are those aramids where the amide linkages are in the para-position relative to each other. In the practice of this invention the aramids most often used are poly(paraphenylene terephthalamide) and poly(metaphenylene
30 isophthalamide).

It is understood that one or more additional fibers or components may be included with the modacrylic and aramid fibers. Two examples

are an abrasion resistant fiber and an antistatic component which may be present as a fiber.

By abrasion resistant it is meant the ability of a fiber or fabric to withstand surface wear and rubbing. Preferably the abrasion resistant fiber is a nylon. By nylon it is meant fibers made from aliphatic polyamide polymers; and polyhexamethylene adipamide (nylon 66) is the preferred nylon polymer. Other nylons such as polycaprolactam (nylon 6), polybutyrolactam (nylon 4), poly(9-aminononanoic acid) (nylon 9), polyenantholactam (nylon 7), polycapryllactam (nylon 8), polyhexamethylene sebacamide (nylon 6, 10), and the like are suitable. The abrasion resistant fiber, if present, typically comprises 2 to 15 weight percent of the yarn.

Illustrative examples of an antistatic component are steel fiber, carbon fiber, or a carbon coating to an existing fiber. The conductivity of carbon or a metal such as steel when incorporated in a yarn, fabric, or garment provides an electrical conduit to assist in dissipating buildup of static electricity. Static electrical discharges can be hazardous for workers working with sensitive electrical equipment or near flammable vapors. The antistatic component, if employed, may be present in an amount of 1 to 5 weight percent of the total yarn.

Yarns of this invention may be produced by any of yarn spinning techniques commonly known in the art such as, but not limited to, ring spinning, core spinning, and air jet spinning or higher air spinning techniques such as Murata air jet spinning where air is used to twist staple fibers into a yarn. Typically the single yarns produced by any of the common techniques are then plied together to form a ply-twisted yarn comprising at least two single yarns prior to being converted into a fabric.

The term fabric refers to a layer that has been woven, knitted, or otherwise assembled using one or more different types of the yarn of this invention. Preferably fabrics are woven fabrics. Most preferably the fabrics are a twill weave.

The dyeing of the flame resistant fabrics is known in the prior art. However in the present invention, criticality is present in the use of a cationic dye with a carrier.

A suitable disclosure of cationic dyes is set forth in USP 4,066,395.

5 Cationic dyes customarily include salts, chlorides, sulphates or metal halides, zinc chloride, salts whose cationic character derives for example from a carbonium, oxonium, sulphonium or ammonium group. Examples of chromophoric systems are azo dyes, primarily monoazo or hydrazone dyes, diphenylmethane, triphenylmethane, methine or azomethine dyes, 10 cumarin, ketone-imine, cyanine, xanthese, azine, oxazine or thiazine dyes. It is also possible to use dye salts of the phthalocyanine or anthraquinone series with an external onium group, for example an alkylammonium or cycloammonium group and also benzo-1,2-pyran dye salts which contain cycloammonium groups. Mixtures of such dyes can also be used.

15 A necessary component in the present invention is a dye assistant. Suitable dye assistants are disclosed in USP 6,547,835. Specifically, these dye assistants are N-cyclohexylpyrrolidone, benzyl alcohol, N,N-dibutylformamide, N,N-diethylbenzamide, hexadecyltrimethyl ammonium salt, N,N-dimethylbenzamide, N,N-diethyl-m-toluamide, N-octylpyrrolidone, 20 aryl ether, an approximately 50/50 blend of N,N-dimethylcaprylamide and N,N-dimethylcapramide, and mixtures thereof.

The dyeing with the cationic dye and dye assistant in an aqueous bath may be undertaken in conventional fashion. Typically the dyeing is undertaken in a temperature range from 70 degrees to 100 degrees 25 centigrade.

However, it is critical in the present invention that the dye assistant is present in a concentration not greater than 15 grams per liter of dye bath. A preferred concentration is not greater than 12 grams per liter and more preferably not greater than 10 grams per liter. Lower concentrations 30 of dye assistant such as below 5 grams per liter will denote a longer dyeing time, assuming all other conditions of the dye process remain the same.

An excessive amount of dye carrier can result in two undesirable properties. A first property is excessive shrinkage of the yarn and fabric. A second property is undue stiffness of the yarn and fabric.

In the following examples all parts and percentages are by weight
5 and degrees in Celsius unless otherwise indicated.

The color and shade depth for the examples were determined by measuring the Hunter 'L', 'a', and 'b' values in the conventional manner. The 'L' color component is a measure of the blackness or whiteness of the sample, while the 'a' value is a measure of where the color of the sample
10 is in the red to green range and the 'b' value is a measure of where the color of the sample is in the blue to yellow range.

EXAMPLES

Fabrics comprising 70 weight percent modacrylic fiber, 15 weight
15 percent meta-aramid fiber, 5 weight percent para-aramid fiber, and 10 weight percent nylon fiber were dyed using a dye and dye assistant in a one step batch process.

The following procedure is set forth for a commercial dyeing process. However, as will be additionally explained below, such
20 commercial dyeing process was modified due to smaller dyeing equipment.

The fabric is loaded into a pressure jet dyeing vessel in which the fabric is circulated through an apertured venturi in a continuous loop achieved by sewing the ends of the fabric together. The fabric is scoured
25 for 10 minutes at 60 degrees Celsius in an aqueous solution of 0.5 grams per liter Merpel® HCS surfactant. After scouring the dyeing vessel is drained and charged with dye, dye assistant, and water at an initial temperature of 70 degrees Celsius. The fabric is dyed for 10 minutes while the bath temperature is increased at a rate of 1 degree Celsius per
30 minute. The pH of the solution is then adjusted by the addition of acetic acid to a pH of between 3 and 4. The vessel is then charged with additional dye and dye assistant and a constant temperature of 80 degrees Celsius was maintained for 10 minutes. The temperature is then

raised as a rate of 1 degree Celsius per minute until the bath temperature is 98 degrees Celsius. The bath is maintained at this 98 degrees Celsius for 60 minutes or until the dye is exhausted. The bath is then cooled to 60 degrees Celsius and drained. The vessel is then charged with a solution of 2 grams per liter sodium hydrosulfite, 2 grams per liter sodium carbonate, and water to neutralize the solution. The bath temperature is raised at a rate of 1 degree Celsius per minute to 60 degrees Celsius and allowed to circulate for 10 minutes. The vessel is then drained and recharged with water. The water temperature is then raised at a rate of 1 degree Celsius per minute to a temperature of 60 degrees Celsius and allowed to circulate for 10 minutes. The vessel is then drained and the fabric dried.

To generate the data below, smaller dye equipment was employed, namely Ahiba Polmat stainless steel canister dye unit (with a heat medium of carbowax).

The dye employed was:

Viocryl Blue RLS dye (ci-41) 0.6% of fabric weight

Viocryl Red AGL dye (ci-29) 0.75% of fabric weight

Yorocryl Yellow 6GL (ci-21) 0.15% of fabric weight.

The fabric described above was prescoured at 60 deg. C with Merpel HCS at 0.5% of fabric weight and Cekogen OX (oxidizing agent) at 3% of fabric weight for 20 minutes followed by cooling, draining and rinsing with water.

The fabric was dyed at a final temperature of 98 degrees Celsius for 60 minutes. The final temperature was reached by an increase in temperature of about 1 degree Celsius per minute. The pH of the dye bath was about 3-4. Aryl ether or benzyl alcohol was used in amounts of 2, 5, 10, 15, 20 and 30 grams per liter. The dye bath was cooled to about 60 degrees Celsius and drained.

The dyed fabric was post scoured with reducing agent to neutralize the dye solution (Sodium Hydrosulfite and Sodium Carbonate at 2 g/l) at 60 deg. C for 20 minutes followed by cooling of the solution and draining.

The dyed fabrics were dried in a moisture teller unit using a hot air blower.

The data below represents shrinkage in % of fabric area at different amount of dye assistants of aryl ether and benzyl alcohol

Dye assistant (g/l)	2	5	10	15	20	30
aryl ether	16	19	22	31	44	84
Benzyl alcohol	17	16	23	25	36	86

The fabric showed excessive shrinkage when dyed at high percentage of dye assistant.

When using dye assistant of more than 20g/l, the fabric also becomes stiff. The dye uptake is also negatively impacted by high percentages of dye assistant as indicated by the following tables of color measurement.

aryl ether(g/l)	2	5	10	15	20	30
L*	29.049	27.838	28.705	30.313	32.302	33.539
a*	2.844	1.962	1.61	0.79	-0.354	-1.091
b*	-10.921	-10.777	-10.216	-9.553	-8.25	-8.186

Benzyl alcohol (g/l)	2	5	10	15	20	30
L*	28.55	26.765	25.987	26.07	28.183	29.228
a*	5.471	6.774	6.289	6.024	4.321	3.093
b*	-33.776	-30.826	-28.07	-26.027	-23.866	-21.713